CALIBRATION OF AN INFRARED SPECTROMETER

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PREFACE

In looking for a research topic the author naturally sought a problem in a field that is of great interest. That field is Spectroscopy. Since the Department of Physics had obtained a new Infrared Spectrometer, this presented an opportunity to do some research in this field.

Since the instrument was new, a calibration of the instrument was necessary before the instrument could be used for any type of infrared analysis. Therefore the general purpose of the research was to calibrate the Perkin-Elmer Model 12A Infrared Spectrometer and to present the procedures used and the data secured in this research paper.

The paper would also be more comprehensive and more readable if a general survey of Spectroscopy, especially Infrared, was presented. Therefore a portion of this paper is devoted to this end.

BRIEF HISTORY OF SPECTROSCOPY

It is not surprising that such a great influence on scientific thinking as Sir Isaac Newton should be the instigator of scientific knowledge which has developed into the modern theory of spectroscopy. Newton was not the first man to notice color due to refraction but he had sufficient curiosity to do something about the problem. This special kind of curiosity which results in the advancement of man's understanding of the material universe is an attribute of all great men of Science.

Whether there is any truth in the story that Newton first observed a spectrum as light streamed through a glass bob on a chandelier is of little consequence in itself. He speculated upon the cause of the colors commonly seen in the rainbow. In his research he conducted one experiment among many which was of profound importance. Securing a glass prism and allowing sunlight, after passing through a small circular aperture, to fall upon the prism he observed the colors produced. Noticing that the length of the spectrum was greater than the width, he surmised that this was due to an unequal thickness of glass or to some irregularities in the glass. Subsequent experiments by Newton proved that the glass behaved a little differently toward each color. He observed that red light was bent less upon passage through a prism than violet light. Thus the fundamental basis of dispersion was discovered. Newton, however, erroneously assumed that this was the cause of spherical aberration and could not be corrected. This, of course, was disproved some time

later. Newton also contributed further to optics in his, then unproved, theories concerning the nature and propagation of light. Newton's influence upon scientific thinking was so profound that for more than a century advancement in optics was almost at a standstill. Huygens'wave theory of light was completely set aside since it was in opposition to Newton's corpuscular theory.

Foucalt proved conclusively that the velocity of light in water is less than that in vacuo. This was a decided blow to Newton's Corpuscular theory and added considerable strength to the Undulatory theory of Huygens. Sometime later Thomas Young in his experiments on interference added more decisive evidence to the wave theory. The work of Young enhanced knowledge and made possible the development of theory leading to the diffraction grating which is of great importance to some forms of modern Spectrometers.

Work in the twentieth century has been confined to the era of modern physics which has contributed such ideas as the quantum theory and wave mechanics. Probably no other single idea has stirred scientific thinking more than the Quantum theory as proposed by Planck. This of course was a direct result of his experiments on radiation by black bodies. He proposed that energy was radiated and absorbed by ideal black bodies in fundamental units called "quanta". This idea is of utmost importance in connection with the radiation and absorption of light due to atoms and molecules. This, along with the earlier work of Balmer on the formula for the spectrum of the hydrogen atom,

aided Neils Bohr to propose his theory of radiation and absorption in the atom. Bohr proposed a planetary atom in which the electrons were arranged in certain discrete energy levels which allowed angular momenta for the electron of integral multiples of $\frac{h}{2\pi}$, where h is Planck's universal constant of radiation. Last, he proposed that radiation was emitted only when the electron moved from a level of higher energy to one of lower energy.

As important as Bohr's postulates were it seems that they just did not explain bright line spectra for atoms other than hydrogen or hydrogen like atoms. It is to be noted that Bohr's postulates are for circular orbits which are the simplest of conic sections. Bohr's theory of the hydrogen atom was extended to elliptical orbits by Sommerfeld. Also this led to the introduction of two quantum numbers instead of the single quantum number needed for Bohr's circular orbits.

Sometime later the Bohr-Sommerfeld postulates were derived by Schrodinger on the basis of his quantum and wave mechanics. Strange as it may seem, the same results were obtained through this more rigorous treatment as were postulated by Bohr. This speaks well for Bohr's ingenuity.

As mentioned above, there were a great number of things that Bohr's theorem could not explain. This was due largely to the fact that Bohr did not attempt to fit his theory to other than the hydrogen type atoms. Subsequent attempts to reconcile theory with experiment have led into a far more complex idea of the electronic structure than Bohr assumed in his original theory.

For example, we now have the idea of the spinning electron which further complicates the over-all picture. The spinning electron figures in the production of fine structure. It is also known that the completed shells of electrons have a decided effect upon the valence electrons by screening them from the nucleus thus altering somewhat the relative motions of the valence electrons.

Over and above what has already been cited, certain external effects were studied. Such effects as the Zeeman and Paschen-Back effects have added much to our knowledge of the atom and the effects of external magnetic fields upon the motions of the electron.

Thus on the basis of the modern theory of the origin of spectra such men as Balmer, Rydberg, Lyman, Paschen and Brackett have been instrumental in laying much experimental groundwork. Then Bohr presented a quantitative treatment of the origin of bright line spectra. From the fundamentals as postulated by Bohr such men as Sommerfeld, Schrodinger, Dirac, Zeeman, Paschen and others have extended these ideas to more complicated systems and have even altered many ideas concerning the atom which were originally proposed by the earlier workers.

As in all things the complex must follow the simple. The ideas concerning the single atom might be considered the simple and interaction of two or more atoms, the complex. Substances may be divided into two great classes: inorganic and organic. Since inorganic substances are easily broken up the atoms there may be studied separately. However, organic substances are often

times so complex that they must be studied as a whole. Historically this is very significant because here again, as many times before, lay a whole unexplored region. This is one of the very wonderful things about science. When a region of endeavor is fully explored other frontiers present themselves. Not that the subject of atomic spectra has been exhausted but rather as an inevitable outcome of this field scientists have naturally sought solutions to the problems of molecular spectra.

The origin of a concerted drive for knowledge in this field might be placed not longer than 25 years back. In fact, the study of molecular spectra is still in its infancy. Much of our knowledge of infrared is a result of the work done by industrial scientists. Through them a great deal of valuable experimental data has been obtained and upon this basis the theoretical scientists have derived much of the theoretical knowledge. Therefore it is not strange to see among the works on infrared a great many written by industrial and research scientists. However, the work of these men must not eclipse the necessary contributions of the great theoretical scientists.

For historical purposes the first serious use of infrared for analysis might be attributed to the petroleum industry. In their search for more efficient products infrared was used in analyzing the various petroleum derivatives. From these research endeavors, a large group of infrared spectrum charts have been obtained.

Following the widespread use in the petroleum industry many other industries have applied infrared to their research

problems. For example, the soap industry used infrared to analyze the long chain fatty acids. Infrared has also been successfully applied to the analysis of many other organic compounds.

If an examination of the electromagnetic spectrum toward longer wave lengths is made the newest field of endeavor is discovered. This is in the region of microwaves. At the present time little has been done in the way of analysis with these waves but here again another new horizon which is full of possibilities presents itself.

In summarizing this very brief history of spectroscopy, a period of extreme activity during the reign of Newton and for sometime after is observed. However Newton's prestige was responsible for an extended lull in development and activity was not again noticeable, to much extent, until the wave theory as proposed by Huygens was able to hold its own. Since then spectroscopy has developed rapidly and still promises a very bright future for this fascinating field of study.

DEVELOPMENT OF INFRARED THEORY

Due to its innate structure a molecule has three types of motion other than motion of translation. The electrons may move from one discrete energy state to another in each individual atom of the molecule, thus giving rise to electronic energies similar to those in atomic spectra. The individual atoms may vibrate with respect to each other which gives rise to vibrational energies. The molecule may also rotate as a whole

about an axis. This gives rise to rotational energies. Thus there are three types of energy; electronic, vibrational and rotational which comprise the total energy of the molecule. Since electronic energies appear in the visible and ultraviolet regions of the electromagnetic spectrum they are not of particular significance in infrared work. Therefore the author will concentrate on vibrational and rotational energies since they do appear within the infrared region.

The infrared region may be divided into four sub-regions. They are: the near infrared, which can be studied photographically; and the infrared proper, which is beyond the photographic region and must be studied thermo-electrically; the far infrared which must be studied in the same manner as the preceding group; and the region of microwaves which needs radar for study in that region. This paper will be concerned mostly with the infrared proper and the far infrared in which the vibrational and rotational energies are found.

It has already been mentioned that the energy of a molecule is divided into three parts. These were the electronic energies, vibrational energies and rotational energies. In comparison the electronic energies are much larger than the vibrational energies and in turn the vibrational energies are far great r than the rotational energies. Thus it would take an instrument of high resolving power to bring out the vibrational effects and one of still higher resolution to make the rotational effects apparent. Plate I is a highly schematic energy level diagram showing the vibrational and rotational levels within the two electronic

states A and B. To one familiar with transitions in atomic spectra it is apparent that any transition from electronic state B to electronic state A would radiate energies found in the visible or ultraviolet regions of the electromagnetic spectrum depending upon the differences in energy levels. Within the vibrational states of a given electronic state a molecule may exhibit overtones as well as the fundamental frequencies. Thus in Plate I a transition from vibrational state one in electronic state B to vibrational state O within the same electronic state would constitute a fundamental frequency. But a transition from the vibrational level two to zero constitutes the first overtone. Due to the energy values represented one would expect vibrational energies to fall in the infrared region. These vibrational levels are further broken up into the various rotational states of the molecule. Transitions between rotational levels within a given vibrational level (G to F, H to G, G' to F', etc.) will produce radiation in either the far infrared or the microwave region depending upon the separation of the levels.

The above discussion seems to give the impression that the molecule is a simple thing. But to the contrary, the molecule is an exceedingly intricate system with a very complex behavior.

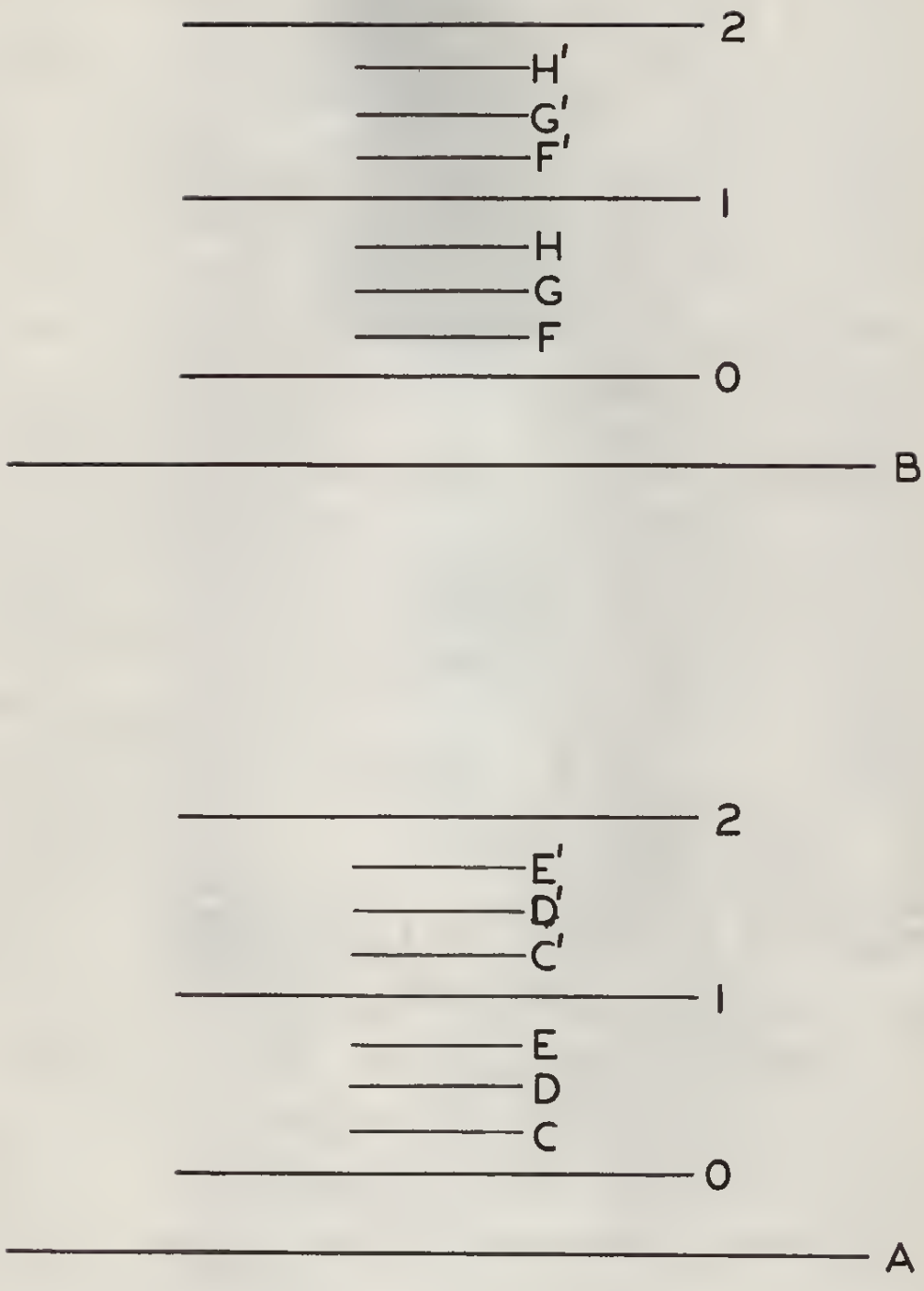
Vibration Spectra

The production of an infrared spectrum hinges upon the fact that the vibration frequencies and rotation frequencies are resonant with the frequency of the incident infrared radiation. In this section a brief account of vibration spectra will be given.

Explanation of Plate I

This plate illustrates an energy level diagram depicting electronic, vibrational and rotational energies. A and B represent separate electronic states. The vibrational states of each electronic state are numbered (0 to 2). The rotational states within each vibrational state are represented by F, G, H, F', G', H', etc.

Plate I



For simple harmonic motion the acceleration towards the origin is always proportional to the displacement. Due to this the frequency of vibration for a harmonic oscillator is given classically by the familiar formula:

$$f_{vib.} = \frac{1}{2\pi}\sqrt{\frac{c}{m}}$$

Where in this case c is a constant for the particular molecule and m stands for the mass of the vibrating particle or, in the case of a molecule, for the reduced mass of the system.

From a purely quantum mechanical standpoint the energy or, more properly, term value for a given vibrational state is given in wave numbers by the following expression:

$$G(v) = \frac{E}{hc} = \frac{f}{c}(v + \frac{1}{2}).$$

In this case v is a vibrational quantum number which takes integral values and which can change only by plus or minus 1. From this basic idea one may derive the expression representing a transition in a given vibrational state from some higher value of v to a lower value of v. Thus:

$$\frac{f_{rad.}}{c} = G(v_2) - G(v_1)$$

$$\frac{f_{rad.}}{c} = \frac{f}{c}(v_2 + 1/2) - \frac{f}{c}(v_1 + 1/2)$$

$$f_{rad.} = f(v_2 - v_1)$$

or

$$f_{rad.} = f$$

Thus it is seen that the radiated frequency $f_{rad.}$ is equal to the vibrational frequency, which is not too surprising. In

general, a given molecule will resonate to only certain incident frequencies which are also resonant with its vibratory frequencies.

Molecules may be linear or non-linear. A linear molecule of n atoms will have 3n-5 degrees of freedom, whereas non-linear molecules have 3n-6 degrees of freedom. Regardless of the complexity of the vibratory motion, it may be resolved into

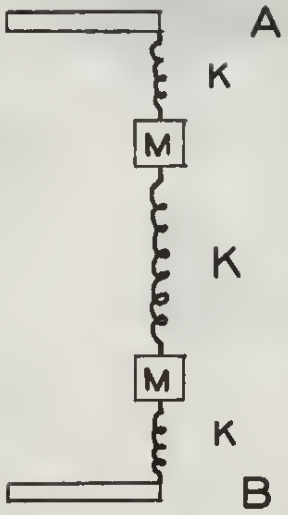


Fig. 1 A simple oscillatory system.

component motions which are called normal modes of vibration. Each of these normal modes of vibration has its own characteristic frequency. As a means of illustrating in a simple way what happens in a molecule in a more complex manner, consider the following problem concerned with determining the normal frequencies and coordinates of a simple vibratory system found in Fig. 1, consisting of two equal masses attached to fixed points A and B by springs of force constant k and to each other

by a third spring of force constant K.

The formulas for the potential energy and kinetic energy of this system are given as follows:

$$V = P.E. = \tfrac{1}{2}kx^2 + \tfrac{1}{2}ky^2 + \tfrac{1}{2}k(x - y)^2$$

$$T = K.E. = \tfrac{1}{2}m\dot{x}^2 + \tfrac{1}{2}m\dot{y}^2$$

where x represents the displacement of the upper mass and y that of the lower. According to an expression due to Lagrange the kinetic energy and potential energy are related as follows:

$$(1) \qquad \frac{\partial}{\partial t}\left(\frac{\partial T}{\partial \dot{q}_i}\right) = -\frac{\partial V}{\partial q_i}$$

If the respective operations on T and V are carried out and equated according to the Lagrange equation the following results are obtained:

$$(2) \quad m\ddot{x} = -[kx + K(x - y)]$$

$$(3) \quad m\ddot{y} = -[ky - K(x - y)]$$

It is possible to represent the displacements, x and y, by the following simple wave equations:

$$(4) \quad x = x_o \sin\sqrt{\lambda}\, t$$

$$(5) \quad y = y_o \sin\sqrt{\lambda}\, t$$

In expressions (4) and (5) the quantity $\sqrt{\lambda}$ actually is used to represent a more familiar quantity called angular velocity which of course when multiplied by t is the phase angle. By taking the second derivatives with respect to x and y, substituting into equations (2) and (3) and eliminating the troublesome factors, $\sin\sqrt{\lambda}\, t$, two linear equations are obtained which may be solved for $\sqrt{\lambda}$ through the use of determinants. The two

expressions so obtained are given in equations (6) and (7) and the determinant follows immediately after the equations:

$$(6) \quad (k + K - m\lambda)x_o - Ky_o = 0$$

$$(7) \quad (k - K - m\lambda)y_o - Kx_o = 0$$

	x_o	y_o	
x_o	$k - K - m\lambda$	$-K$	$= 0$
y_o	$-K$	$k - K - m\lambda$	

The solution of this determinant yields a quadratic equation whose roots λ_1 and λ_2 are easily found by factoring. These roots are given in equations (8) and (9):

$$(8) \quad \lambda_1 = \frac{k}{m}$$

$$(9) \quad \lambda_2 = \frac{2K + k}{m}$$

As already mentioned the $\sqrt{\lambda}$ is the angular velocity. Therefore it is possible to find the two normal frequencies which are given in equations (10) and (11).

$$(10) \quad f_1 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$(11) \quad f_2 = \frac{1}{2\pi}\sqrt{\frac{2K + k}{m}}$$

In regard to the normal coordinates, they may be determined by equating the ratio of the amplitudes to the ratio of the corresponding minors of the determinant. Thus one sees that for λ_1 the ratios are positive and for λ_2 the ratios are negative. This indicates that in the former case the coordinates are such

that the two masses vibrate in the same direction, and in the latter case the vibrations would oppose each other.

In summarizing this problem it is noticed that when displacement of the two masses is in the same direction the normal frequencies depend only upon the force constant k and the mass, whereas, if they are displaced oppositely the force constant of the inner spring enters the expression. This is a simple example of a phenomenon very complex in an actual molecule. However, this method of solution is applicable to the molecule. Part of this complexity in molecules is due to the fact that a molecule generally is not a harmonic oscillator. One would expect that for a simple illustration as that used the first overtone frequency would be twice the fundamental frequency. For molecules, however, certain higher order terms alter the picture. In other words, the molecule is essentially an anharmonic oscillator. This fact would tend to alter the frequency of the first overtone to a little less than twice the fundamental frequency.

Rotation Spectra

If one could consider a rotating molecule as having its atoms at a constant distance from the geometrical center he would have a rather simple case but due to the fact the molecule is not rigid the rotational energies will be somewhat affected by the vibration. However, according to classical mechanics, neither one would produce radiation without an unbalance of electric charge on the atoms. In other words, molecules that

do not have a dipole moment, such as oxygen, do not produce vibrational or rotational energies but only electronic energies which appear only in the visible region. Due to this dipole moment for molecules that absorb or radiate in the infrared region, the radiated frequency, or absorbed frequency are affected by the rotating field as lines due to electronic transitions are affected by a weak magnetic field. Of course, the vibrational frequencies will also be affected by this rotating field.

According to classical mechanics the rotational energy E is proportional to the rotational inertia I and the square of the angular velocity w. Thus:

$$E = \frac{1}{2} I w^2$$

The rotational momentum L is given by the product of the rotational inertia and the angular velocity. Thus:

$$L = Iw$$

From the two preceding expressions the energy, according to classical mechanics, is given by the following expression.

$$E = \frac{L^2}{2I}$$

On the basis of quantum mechanics it can be shown that the angular momentum is determined by the rotational quantum number J in such a way that

$$L = \sqrt{J(J+1)}\ h/2\pi$$

which gives the following expression for the energy.

$$E = \frac{J(J+1)h^2}{8\pi^2 I}$$

In these expressions h is Planckε' constant of radiation and I is the rotational inertia of the system. The rotational quantum number J can take all integral values including zero.

Interaction of Rotation and Vibration

The study of infrared spectra would be relatively easy if the molecule could be considered either a rigid rotator or a harmonic oscillator. Unfortunately a molecule cannot behave just as desired. Consequently the infrared spectrum of a given compound is somewhat complicated by the fact that superposed upon the more pronounced vibrational energies we have the rotational energies. This could be likened to the fine structure so common in atomic spectra. Thus, a more complicated molecular model must be assumed. This model must vibrate and rotate simultaneously.

Thus for the vibrating rotating molecule, the complications involved can be visualized. For a diatomic molecule, this rotation would take place around an axis perpendicular to the lines joining the atoms. For more complex molecules, this axis may be in any one of several planes. This of course brings up the idea of symmetry which the writer believes is beyond the scope of this paper. Therefore it is found that the total energy for the vibrating-rotating molecule from an empirical approach is given as follows:

$$W = E_v + \frac{J(J+1)h^2}{8\pi^2 I}$$

The J values are the same as for the previous discussion on rotation. An analysis of the spectrum of vibration and rotation shows the lines to be equally spaced with the absence of the $J' - J'' = 0$ line. The first lines that do appear are spaced at an interval of 2B on either side of the missing central pure rotation line.

In summarizing vibration and rotation spectra it might be said that for a beginning the molecule may be considered as a harmonic oscillator but this must be altered by certain anharmonic terms in order to fit empirical conditions. The molecule then was considered as a rigid rotator but of course under actual conditions the molecule both vibrates and rotates. On top of this vibration-rotation spectra terms due to the interactions must be added. Thus, within the scope of these few pages, the complexitiss of the vibrating-rotating molecule can be understood.

Raman Spectra

When a strong beam of light is allowed to fall upon a colloidal solution each colloidal particle reflects the beam. This is called the Tyndall effect. The reflected beam has the same frequency as the incident beam according to the laws of Rayleigh Scattering. It was noticed however on each side of the line caused by scattering two equally spaced lines produced by oscillation and many finely spaced linss between due to rotation.

This is explained by the fact that the electric field of the incident light wave produces a dipole moment of vibration and rotation. In order for a molecule to emit or absorb in the infrared region it must have a dipole moment. This of course means that such molecules as oxygen and hydrogen do not radiate energy normally in the infrared region but do present Raman lines. Light seems to have a duo-personality. For example, it oftentimes behaves as an electromagnetic wave, at other times as a quantum of energy, the light photon. As a photon it can interact with a molecule or atom in several ways. If elastic collision takes place there is simple Rayleigh Scattering. If, however, the photon gains energy from the molecule or loses energy to the molecule there would appear on either side of the Rayleigh line a line of higher frequency and a line of lower frequency. From the classical viewpoint the dipole moment set up may cause an electron to jump from a lower to higher energy state thus absorbing energy or it may cause an electron to fall to a lower energy state and emit energy thus accounting for the displaced Raman lines. This would also account for the Raman Spectra of the non-polar molecules. Classical theory shows that the displaced vibrational lines are displaced about twice as much as the infrared lines. Also experiment has revealed that there is e tendency for the Raman line toward the lower energy value to be missing. This is explained as follows: molecules are always in a state of thermal agitation, thus it is found thet usually the molecule will be in a higher energy state.

Therefore, the probability of a molecule being in the higher energy state is greater than for the lower energy state. Thus one would expect the line toward the longer wave lengths to be observed more often than those toward the shorter wave length side.

Raman spectra is especially useful in the study of the vibrational frequencies in non-polar compounds which do not give rise to energies in the infrared region.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

The techniques and procedures of infrared spectroscopy are far from being standardized. This is, of course, generally true in all comparatively new fields. However it is interesting to note that certain experimental ideas apply in general to the whole of spectroscopy. For example, a question to be answered might be, what make of instrument should be used?; should it be a grating or prism instrument?; what kind of light source should be used?; and what type of detecting and recording device should be used? No attempt will be made to give positive answers to these questions but some attempt will be made to present various possible solutions.

The choice of infrared spectrometers is somewhat limited. Most observers have, in the past, preferred to develop their own. In spite of this apparent shortage of good commercial instruments there have been several instruments that have been proven successful. One of the most successful has been the instrument

developed by the Perkin-Elmer Corporation. This instrument was used in the research for this paper.

Dispersive System

Most of the prism spectrometers are of the littrow type in which the light is doubly dispersed before it reaches the detecting device. Since glass is opaque to radiation in the infrared region the dispersing agent is either a rock salt, Potassium Bromide or Lithium Fluoride prism depending upon the region to be investigated. If all three are used, a region almost 25 microns in width may be investigated. In general the rock salt prism is the best since it covers the range from 2.5μ to 15μ and is also the most economical. The grating instrument is superior to the prism instrument if higher resolution is desired since the theoretical resolving power is proportional to the number of lines. However, the spectrum produced by a grating is much less intense than that produced by a prism. One would probably be safe in saying that for high resolution and low intensity use a grating; for high intensity and low resolution, use a prism. One of the chief difficulties with prisms is that the growing process must be carefully controlled in order that the best crystals may be obtained. Due to these possible imperfections the theoretical resolving power is seldom achieved. According to Sawyer (10) some prisms have been made which do reach very nearly the theoretical resolution.

Source

Another very important aspect is the type of light source to be used. The choice of a source of radiation must be carefully

made. The source must radiate in the desired region and must be electrically stable so that it produces a uniform radiation. Also most sources are subject to some atmospheric instability. The source should retain its stability through ordinary changes in atmospheric conditions. If it does not, radically different results might be obtained even over a relatively short period. Most black body radiators emit radiation in the near infrared. A typical example is a heating element as used on electric ranges. However this type of element does not approach black body conditions as well as others. An element of this type which is somewhat closer to a black body is the globar heater which is used in the Perkin-Elmer instrument. Another good source of infrared is the Nernst glower. This source is composed of zirconium oxide with a suitable binder. It operates at about the same temperature as the Globar, but is, in general, not as rich in radiation beyond 15 microns as is the globar. It seems that if instruments are to be made commercially that the radiator chosen should be as stable and as nearly black as possible and still be easily handled and economical.

Detectors

Next to the dispersing medium probably the detecting device should be considered. Probably this is sufficiently important to merit considerable thought. The detecting device converts small temperature changes into small electrical currents which are fed either to a recording galvanometer or a sensitive galvanometer which causes a light spot to pass over a screen

and the subsequent deflections observed. The detector is a radiometric device such as a radiometer, bolometer or thermopile. The radiometer is probably the most sensitive but due to its construction it is not as practical as the more rugged thermopile. Hence, the thermopile is used because of its construction and ease of use. The junctions of the thermopile are oftentimes made of bismuth and bismuth-tin alloy. The bismuth is sputtered or evaporated on a thin strong base such as glass or shellac. The junctions are normally fastened to four heavy copper leads which conduct the thermal current to the recording device. The thermopile is sealed off and evacuated to as much as 10^{-6} millimeters of mercury. To facilitate this high vacuum the thermopile is oftentimes baked out with activated charcoal. The thermopile will in general hold its vacuum over a considerable period of time. The vacuum is maintained by a charcoal trap which after baking, is kept at a low temperature, generally with liquid air. The sensitivity of the thermopile is somewhat increased with the low pressure produced. In order to compensate for drift oftentimes another pair of junctions is wired in opposition or a small resistance is used as a shunt in order to reduce the second order effects due to fluctuations in the thermal current. Another useful device for detecting radiant energy is the bolometer. It consists generally of blackened platinum strips or wires which are placed in the path of the radiant energy. The energy is absorbed and raises the temperature of the strips. This rise in temperature produces a change in the resistance of the

stripe. With instruments that are sufficiently sensitive, this change in resistance can be measured quite accurately and thus the amount of energy can be determined.

Sample

Another extremely important aspect of infrared analysis concerns the techniques of sample preparation. Since samples may be either liquid, solid or gaseous the construction of the absorption cell is extremely important. The construction of the absorption cell for liquids is somewhat more difficult than for gas cells. The main thing is that the windows used for the cell should be insoluble in the liquid under analysis. This is particularly important when water is used as the solvent. The windows should, of course, transmit in the region under consideration. Typical materials for cell windows are glass and quartz for the near infrared and calcium fluoride, sodium chloride, potassium chloride and potassium bromide for the infrared. The liquid cell is generally constructed of windows separated by a lead foil spacer and held together by a clamp. It can be shown that the amount of incident radiation transmitted is dependent upon the concentration of the sample and the length of the optical path. Thus the greater the concentration and the longer the path the greater the absorption. This is the well known Beer's Law.

Gas absorption cells are similar to liquid cells in design. Approximately the same precautions must be taken in the choice of windows. The windows are separated by a glass tube which frequently carries two sidearm tubes. One is used for the evacuation of the cell and the other to introduce the sample to

be analyzed. The writer will have more to say concerning the construction of a gas absorption cell later. It is interesting to note that the transmissivity of a gas depends upon the pressure. An increased pressure effectively increases the concentration, thus increasing the amount of absorption.

The construction of absorption cells for solids poses a somewhat more difficult problem. Solids have to be treated much in the same way as liquids. In general, the sample thickness is small usually not more than a few millimeters and oftentimes is much less than one millimeter. The difficulty is that in order to faithfully repeat the performance of the cell the sample thickness should be repeatable to within five percent. The cell itself generally consists, of two windows, made of the desired material, which are separated by spacers of the required thickness. They are then either clamped together or four small nuts and bolts are used, one in each corner. The spacers are used so that the sample thickness may be repeated faithfully. Since the reproduction of the sample thickness is so important the preparation of the sample should also be considered. If the sample is fusible, oftentimes it may be spread upon one of the windows and pressed to the required thickness. If the sample is soluble it may be handled the same as for liquids. If it is not fusible or soluble it may be mulled in nujol.

A person can easily understand and appreciate some of the problems facing the research in infrared. As it stands at the present time research is very much individualized. A few of the techniques are standardized, but the majority are not. Whenever

research calls for the personal touch it seems to become very challenging. A few of the trials and tribulations of research the writer is saving for the discussion of the research problem.

DESCRIPTION OF THE PERKIN-ELMER INFRARED SPECTROMETER

Before discussing the methods of adjustment and calibration of the Perkin-Elmer Infrared Spectrometer a description of the working parts of this instrument is in order. An external view of the instrument is shown in Plate II. Plate III consists of a photograph and schematic diagram showing the essential working parts.

Source of Radiation

The source of infrared radiation was a globar heater. This heater is composed of a silicon carbide rod which is generally operated at temperatures between 1000°c. to 2000°c. The rod is held between aluminum electrodes and mounted in a water cooled jacket. The globar is an extremely useful source of infrared, particularly in the wave length regions investigated.

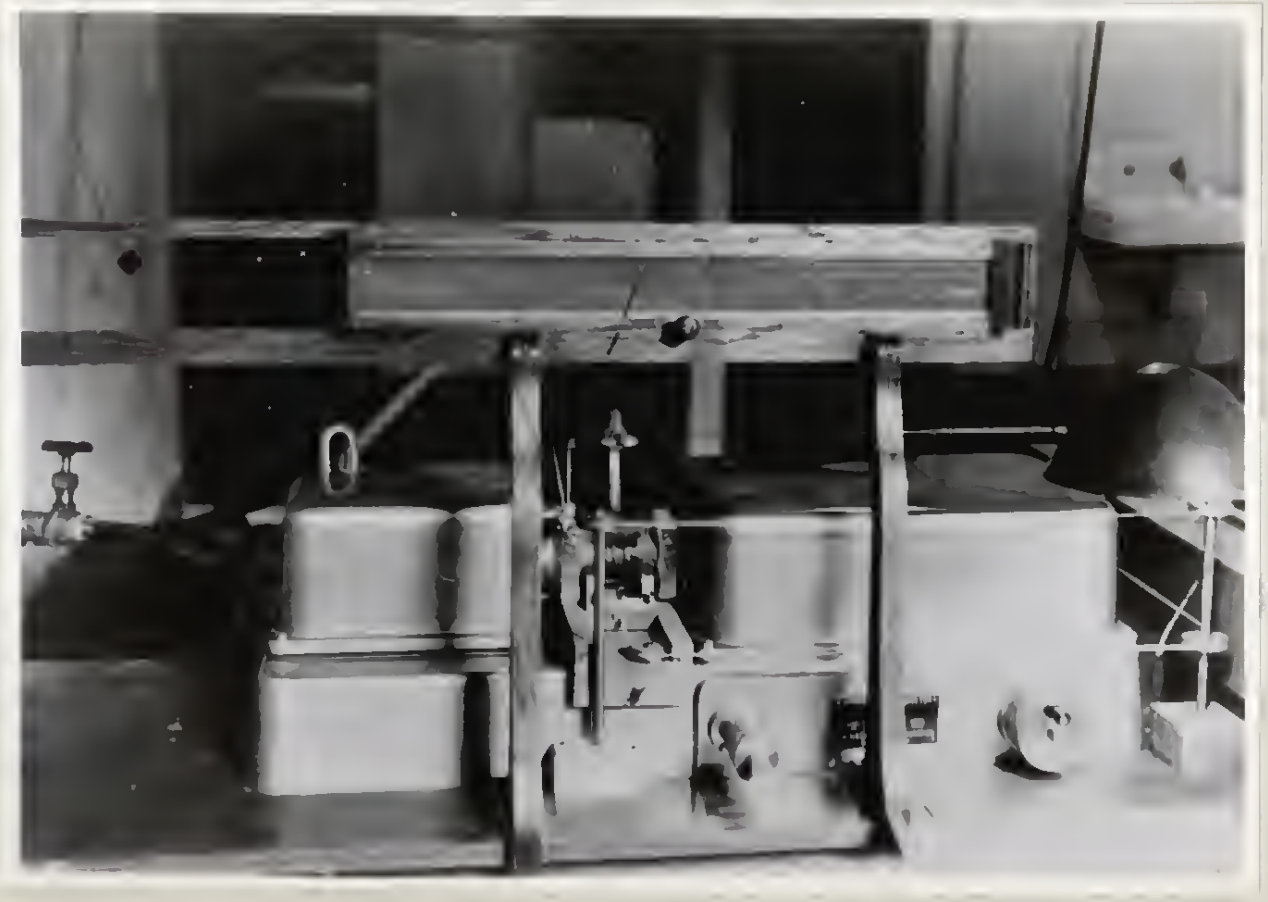
Dispersing Agent

The dispersing system in the Perkin-Elmer Spectrometer consists of a sixty degree rock salt prism. The mounting of the prism is of the Littrow type. The rock salt prism is probably the most effective material for most work, since the approximate range of such a prism is from 2.5 microns to 15 microns. In case the range is to be extended both potassium bromide and potassium fluoride prisms may be obtained.

Explanation of Plate II

An exterior view of the Perkin-Elmer model 12A infrared spectrometer.

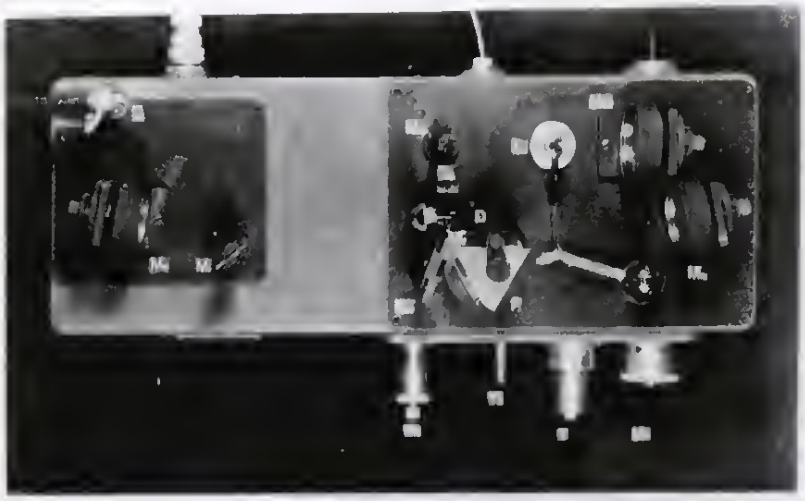
Plate II

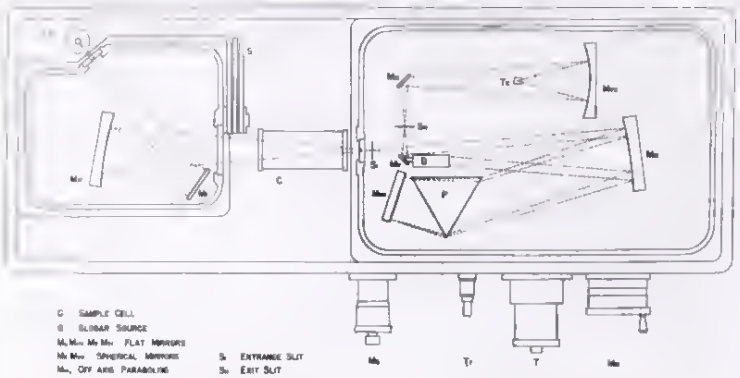


Explanation of Plate III

A view of the working parts of the Perkin-Elmer infrared spectrometer with an accompanying schematic diagram.

Plate III





C SAMPLE CELL
G GLOBAR SOURCE
$M_1 M_{11} M_9 M_{11}$ FLAT MIRRORS
$M_5 M_{10}$ SPHERICAL MIRRORS
M_{12} OFF AXIS PARABOLOID
M_8 SLIT MICROMETER
M_6 WAVELENGTH MICROMETER
P PRISM
S SHUTTERS
S_1 ENTRANCE SLIT
S_2 EXIT SLIT
T TURRET DRUM
T_r TURRET RELEASE
T_c THERMOCOUPLE
θ TEMPERATURE COMPENSATOR

PERKIN-ELMER INFRARED SPECTROMETER
MODEL 12A

Detector

The Perkin-Elmer infrared spectrometer has a high vacuum compensated thermocouple. The junctions are made of bismuth and bismuth-tin alloy. The junctions have an effective area of 2.4 millimeters^2 with a total resistance of twelve ohms. The thermocouple has a compensation of about ninety five percent for the fluctuations in the thermal current. An examination of the properties of the thermocouple in the Perkin-Elmer spectrometer impresses a person with the obvious versatility of this instrument. This actually becomes more apparent when one considers that the rated resolution of the instrument is the separation of the doublet in the 4.2 micron band of carbon dioxide. It is also interesting to note that the wave length can be reproduced within one tenth of a scale division on the micrometer drum and that the energy can be reproduced to one percent at a slit width of .03 mm provided the settings are immediately repeated.

Recorder

The choice of a recording device is a task that also bears considerable consideration. When the research was done for this paper a Leeds and Northrup table galvanometer was used. This instrument has a high sensitivity which ranges from one ten thousandth of a microampere to about five thousandths of a microampere depending upon the resistance of the instrument. Due to this high sensitivity any small fluctuations in the thermal current may cause rather serious drifting. Also building vibrations tend to cause both vertical and horizontal vibrations which may be somewhat bothersome. Muller has developed a vibration free suspension which was utilized in our case. A reference

to this suspension can be found in Strong (12). The main thing is that the system should have a natural period different from that of the surroundings. Since the suspension does have a natural period of its own it is necessary to provide for damping. In Muller's method a number of pie pans filled with oil and placed one on the other is used. The damping action is due to the internal friction of the oil.

The current from the thermocouple is fed to the galvanometer through shielded cables to prevent induced currents from external fields. This thermal current produces a deflection of the galvanometer coil which is proportional to the current received. Since the current produced is directly proportional to the energy of the incident radiation upon the thermocouple the galvanometer deflections are therefore also proportional to the amount of incident radiation received at the thermocouple. Since our galvanometer was not a recording type it was necessary for us to observe the deflections by means of a spot of light which after several reflections was observed on a ground glass scale. Even though the period of the galvanometer is commensurate with the period of the thermocouple it does take considerable time to run an absorption curve by this method. An automatic recording galvanometer would be a great time saver.

ADJUSTMENT

There are some adjustments that must be made. Probably the most important of these is the adjustment of the paraboloidal mirror which reflects the light into the prism. This mirror

serves as the collimator of the optical system. The use of mirrors in the infrared is necessitated by the opaqueness of glass lenses. Also due to the fact that chromatic aberration is absent in mirrors, this is of course an argument in favor of the mirror. However, the problem of spherical aberration is still present. This can be somewhat alleviated by using parabolic mirrors, although not necessarily completely. According to Strong (12), one of the most satisfactory arrangements is an off axis paraboloid. This eliminates the use of a plane mirror to deflect the light into the prism as in the method by Pfund. The use of a paraboloid necessitates careful adjustment of the mirror, with respect to the entrance slit in order to collimate the rays. Also the axis of the mirror must be carefully adjusted so that as much of the incident energy as possible be returned to the thermocouple detector. This would be extremely vital in the case of an off axis paraboloid. The initial adjustments of the parabolic mirror were made through the use of the 4.3 micron band of carbon dioxide. The mirror was rotated by very small amounts; generally not more than one degree. A check was then made on the carbon dioxide band. This process was repeated until a close approximation to the accepted absorption curve was obtained. Whether or not the right mirror setting was obtained could be checked easily by running the absorption curve with the mirror rotated say a half degree to the left of the accepted position and then to the right of this position. If the best adjustment had been obtained definite deviations would be observed. It was not expected that perfect reproduction would

be obtained because of dissimilar conditions under which the original curve was obtained.

CALIBRATION

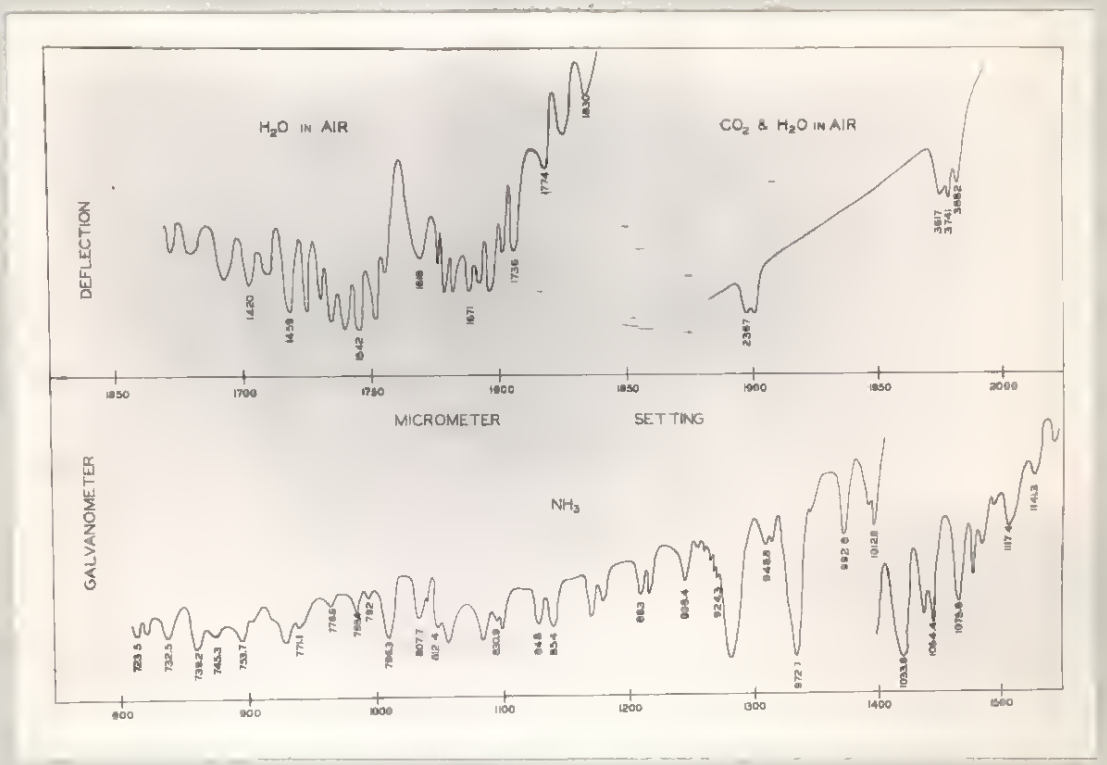
The prime prerequisite before a new instrument can be used is that it must be calibrated. This calibration is for the purpoee of determining the behavior of the instrument. In the caee of an infrared spectrometer thie calibration should indicate how faithfully the inetrument will reproduce certain known absorption curves. It should also give an indication of the diepereion and the reeolving power of the instrument. The methods of calibration are very nearly standardized. It coneists of checking point by point the known absorption curves for certain substances that cover the tranemission range of the diepersing agent.

The first absorption curve for calibration purpoees was the 6 micron water band. This particular curve is not extensive falling between 1200 wave numbers on the long wave length end to 2000 wave numbere on the short wave length end. In spite of the brevity of the band four hundred points were determined in order that sufficient resolution could be obtained. This made poseible a sufficient number of good calibration poi ts. The only linee that were used were those that were conspicuous. The absorption curve for water vapor is to be found in Plate IV. One of the very curioue aspecte discovered in running through the band wae the fact that the entire band should be worked through at one sitting,

Explanation of Plate IV

This plate consists of the three absorption curves which were used for calibration purposes.

Plate IV


H_2O IN AIR
CO_2 & H_2O IN AIR
DEFLECTION
1420
1459
1542
1671
1736
1774
1830
2357
3617
3741
3862
1850
1700
1750
1800
1850
1900
1950
2000
MICROMETER SETTING
GALVANOMETER
NH_3
723.5
732.5
738.2
745.3
753.7
774.1
784.6
792.1
794.3
807.7
812.4
838.9
848.8
854.4
883
895.4
924.3
948.8
972.1
992.8
1012.8
1033.6
1064.4
1078.8
1117.4
1143.3
800
900
1000
1100
1200
1300
1400
1500

for example, one half of the curve was run one day and the other half the next day. When the two parts were placed together they did not fit. This undoubtedly was due to the difference in conditions under which the two were run. Any fluctuations in atmospheric conditions would affect the results. Due to this possible difficulty it was found that much better results could be obtained if the entire band was run during the night. When this was done the absorption curve obtained compared favorably with the accepted curve. By plotting wave numbers against micrometer drum setting a calibration curve was obtained. This curve should be smooth. When a complete calibration is obtained from the minimum to maximum drum setting the ends will vary from linearity. The calibration curve is to be found in Plate V. The first conclusion to any decided deviation from a smooth curve, is that adjustment of the instrument is not accurate. The writer says this, knowing that irregularities in the prism or other faults in the optical system are not likely to be present. A second thought is to be found in an article by Paul C. Cross (5) of the University of Wisconsin. He found that it was necessary to apply a temperature correction to the index of refraction of a rocksalt prism. Any marked changes in temperature would produce fluctuations in the angle of minimum deviation which of course would affect the dispersion of the prism. There would also be a decided loss in definition and resolving power. In the light of these considerations, changes in temperature could be easily responsible for observed irregularities of the

calibration curve. When the absorption curve for ammonia was obtained the work was done at night to reduce effects of temperature changes and to complete the curve at one sitting.

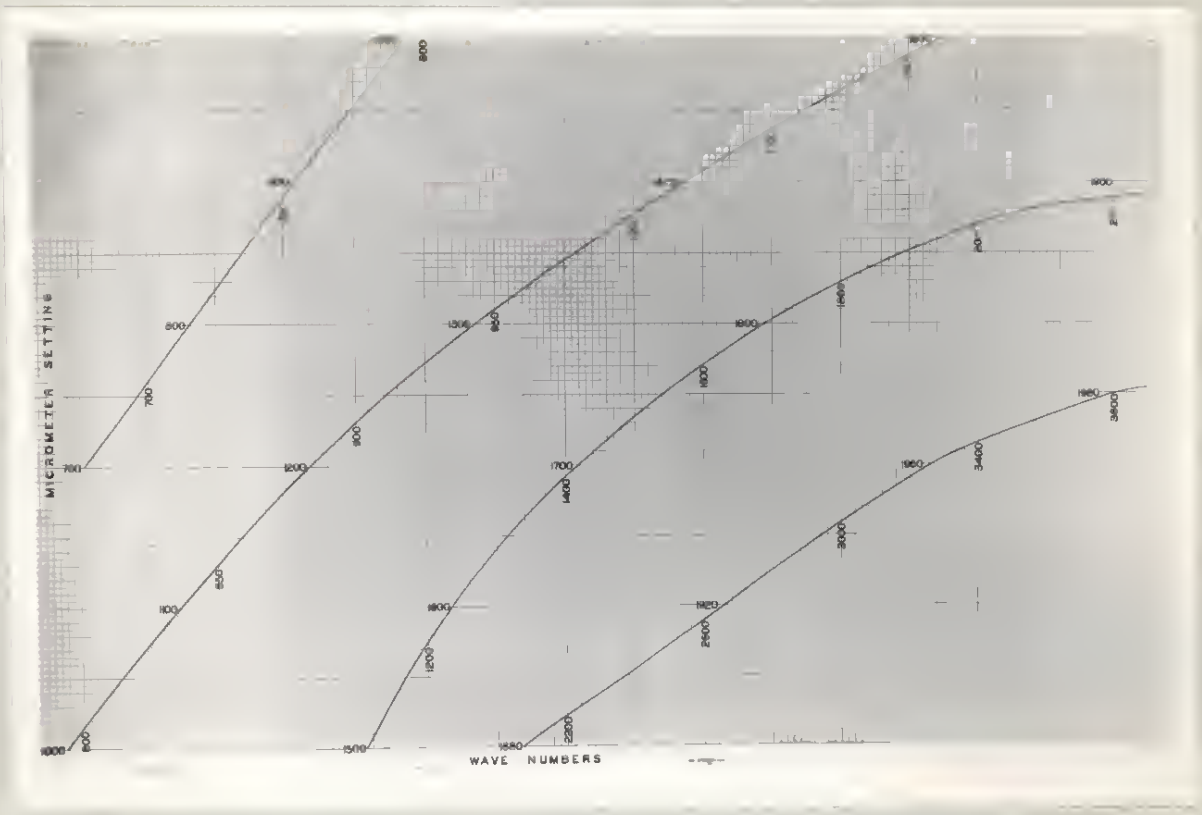
Preparations for the ammonia curve were somewhat more difficult. An absorption cell had to be made and a means of evacuating the cell and introducing ammonia had to be developed. The absorption cell was constructed of pyrex glass tubing. The windows were of rock salt. The cell was 10 centimeters long and 5 centimeters in diameter. Dr. Robert McFarland of the Physics Department expertly welded a side arm tube onto the cell. The rock salt windows were approximately one and a half centimeters thick. The task of grinding the rock salt plates was a long one. The plates were rough ground with various grades of carborundum and finally polished with Jewelers rouge. In this case it was not necessary that the windows be optically flat but they were polished to the extent that they were very transparent. The windows were sealed to the cell with a mixture of resin and beeswax. The cell was mounted on the spectrometer upon a track built by Professor Floyd of the College. Thus the cell could be moved in and out of the radiation beam. The cell was just long enough to fit between the two housings on the spectrometer. This eliminated as much of the air path as possible preventing any atmospheric absorption.

The ammonia generator and vacuum apparatus though not particularly difficult in design did involve some rather tricky glass work. The essential parts of the apparatus were the generator,

Explanation of Plate V

This plate consists of the calibration curve for the Perkin-Elmer infrared spectrometer. It has been divided into 4 parts for ease of handling.

Plate V



a means of evacuating the cell and introducing ammonia and a manometer for regulating the gas pressure to about 10 centimeters of mercury. The ammonia gas was produced with ammonium chloride and sodium hydroxide according to the following equation:

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH \longrightarrow NH_3 + H_2O$$

The ammonia absorption curve was plotted by taking the deflections for every quarter division on the micrometer drum. This meant approximately 800 points and took about 15 hours to run. This seems to be rather laborious but when you consider how close some of the absorption lines were it certainly was the best procedure. This becomes more strikingly apparent when two lines only three wave numbers apart would have been missed. An examination of the absorption curve for ammonia, as seen in Plate IV, shows that the dispersion increases towards the shorter wave lengths. The calibration curve in Plate V also makes this point clear. When the calibration curves for both water vapor and ammonia are placed together, the resultant curve agrees favorably with the accepted curve as furnished by the Perkin-Elmer corporation. Thus one sees that the curve is linear over a great portion of the curve but deviates from linearity toward the shorter wave lengths. An approximate dispersion for this instrument over the straight portion of the calibration curve is 3.5 microns per drum division.

Time would not permit further attempts at calibration. If an absorption curve could have been obtained for Methane a calibration probably would have been obtained which covered a larger

part of the low wave length range of the instrument. However, this would have necessitated the purchase of both potassium bromide and Lithium fluoride prisms. Thus, the calibration was limited to the range of the rock salt prism which was used. In spite of the limitations imposed upon the research, the results were definitely favorable.

INFRARED AS AN ANALYTICAL TOOL

The previous chapter on infrared theory brought out the importance of its use in organic analysis. Pioneer investigators found that the frequencies of vibration and rotation of the atoms of a molecule were commensurate with the frequencies found within the region of infrared radiation. This awakened interest in this field. Many accomplished spectroscopists set out upon the task of acquiring more knowledge. The interesting thing about those participating in the early work was that for the most part they were industrial scientists. Thus it was through the scientists working in industry that infrared was brought into its own. All of the research apparatus was developed to suit the individual investigator with no thought of developing a precision spectrometer for general use in the laboratory. However, such instruments are available now and with such tools a great deal of research can now be done in most institutions.

Since a great many compounds, and in particular organic compounds do absorb characteristically in the infrared, an invaluable analytical tool presents itself. As a means of determining structure a great deal of work has been done on the more

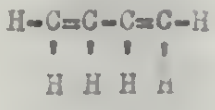
simple molecules. Among the simpler molecules might be included methane, acetylene, ethylene, and their halogen derivatives. Some molecules, due to their symmetry are fairly simple. Chief among this type is benzene and its simpler derivatives. In general, the atoms of a molecule may vibrate in one of two directions relative to the valence bonds. Thus vibration may be perpendicular to the valence bond or parallel to the valence bond. Since the conditions for vibration are different in each case, absorption for these types of vibratory states should be different. Thus it is possible to distinguish between them by comparing their absorption curves. This is not of particular interest to the chemist who is concerned with structure but it is of importance to the physicist who is interested in the relative motions of the atoms. From this knowledge he can determine the necessary equations governing these vibrations. These equations are in general the familiar equations of simple harmonic oscillators, although the motions may be complicated by the space arrangement and the type of bonding between the atoms. Since rotation is taking place the absorption curve becomes very much more complicated. Under low dispersion the rotational effect appears as a broadening into a band rather than as a single frequency.

As already mentioned the chemist is chiefly concerned with structure rather than the motions of the molecule. For example, it would be important to the chemist if he could determine the difference between a normal compound and a substitution product. It becomes more of use to him if he can determine the atom upon

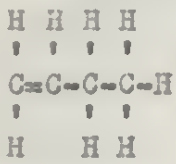
which the substitution is made. For example, it is important to know whether chlorine is substituted on the second or third carbon atom of normal pentane. Experiment has shown that the absorption curves for these substituted products are slightly different. Another example is the difference between 2,2,4 trimethyl pentane and 2,3,4 trimethyl pentane. Both have a deep absorption line at 1460 cm^{-1} and another at 1360 cm^{-1}. The difference is the fine structure of the 2,2,4 product in the absorption curve at 1360 cm^{-1} as well as decided fine structure in other positions along the absorption curve which is absent in the 2,3,4 product. It is also interesting to note that isomers also absorb differently. For example, normal decane has quite a bit of fine structure whereas isodecane has practically no fine structure. There is a marked difference between normal dodecane and isododecane. There are relatively deep absorption lines in the isomer that do not appear in the normal compound. Thus, it is that isomeric differences may be detected by comparing absorption curves.

A number of organic compounds have double bonding between carbon atoms. It is interesting to note the differences in the absorption curves of butene-1 and butene-2. The double bond in butene-1 is between carbons one and two, whereas, for butene-2 it appears between carbons two and three. Although the absorption lines are in the same position, those for butene-2 are broader and exhibit quite a bit more fine structure within each deep absorption line. A great number of the longer chained hydrocarbons

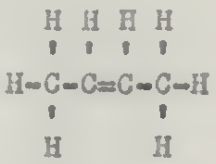
contain more than one set of double bonds. Oftentimes these double bonds are conjugated. This means that the double bonds lie on adjacent carbon atoms. For example consider the conjugated double bonds in butadiene, the formula for which is given as follows:



Actually butadiene is somewhat similar to both butene-1 and butene-2. For comparison purposes the structural formulas for butene-1 and butene-2 are given as follows:



Butene-1

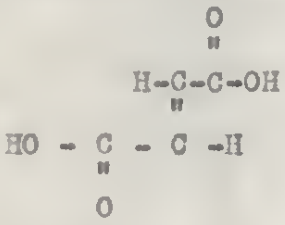


Butene-2

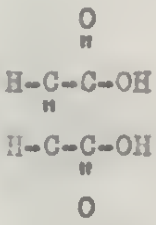
Thus the difference, structurally, is the additional double bonds of butadiene with the necessity of dropping two of the hydrogen atoms. It seems that carbon atoms connected by a double bond act as resonators whereas those tied together with a single bond act as a buffer, or seem to absorb the vibration. Therefore the absorption curve for a conjugated system will be very different as compared with the absorption curve of an unconjugated system. An examination of the absorption curves for these compounds as found in the book on infrared spectroscopy by Barnes, Gore, Liddel and Williams (2) reveals this to be true. The addition of an element to the conjugated butadiene should yield the same compound as a substituted product of either butene-1

or butene-2. Thus it should be possible by comparing absorption curves to determine upon which conjugated carbon atom the element was added. This would be of decided value in determining the chemical properties of the conjugated compound through the use of a physical tool.

A large number of compounds have the same molecular formula and chemical properties but differ in their space configuration. In organic chemistry these are termed cis and trans compounds. Very little has been done in the use of infrared for determining whether a compound exists in the cis or trans stage. This is apparently a wide open field for research. In order to distinguish between cis and trans formations the formulas for fumaric acid and maleic acid are as follows:



Fumaric Acid



Maleic Acid

Fumaric acid and maleic acid are identical compounds except for the space configuration. Thus fumaric acid is the trans compound and maleic acid is the cis compound. It certainly seems that the relative positions of the resonating $C(=O)-OH$ groups would introduce differences in the absorption spectra of these compounds. The writer has been unable to find references to these absorption curves.

The reader can certainly visualize the unlimited possibilities that infrared presents in the analysis of organic compounds. Not only is infrared useful for structual analysis in the laboratory but is has found widespread use for qualitative analysis, in industry. Particularly so in the petroleum industry. When crude oil is refined a great number of by-products are obtained. This group of by-products is generally oomposed of compounds belonging to the methane series of hydrocarbons. In this group are found gasoline, kerosene, vaseline, parafin, and other light and heavy oils. With infrared both a qualitative and a quantitative analysis could be run. From a qualitative standpoint it would be possible to detect evidences of several compounds in a mixture or to determine the purity of a desired product. For example, if the amount of parafin in motor oil is desired, the infrared absorption curve could be obtained and compared with a curve for the same compound with a known amount of parafin present. It should also be possible to determine the octane number of gasoline in a similar manner. The octane number is defined as the percent of 2,2,4 trimethyl-pentane present in a mixture of that compound with normal hexane. Actually it is a well known fact that each component of a mixture will absorb characteristically. Thus, all that remains is to choose the frequencies for which one component absorbs and the others do not and compare with the absorption curve of the entire mixture. The concentration of each component can be found by the solution of simultaneous equations set up from Beer's Law. It is first necessary to

determine the percent transmission for each pure component and then compare this with that of the mixture at the prescribed frequencies. Thus infrared can be used for quantitative analysis even though it was first considered to be applicable only to qualitative analysis.

In the book by Barnes, Gore, Liddel and Williams (2), a very interesting disoussion is found concerning quantitative analysis. They give a number of concrete methods for analysis. Particularly interesting is their discussion on multicomponent analysis. For example if a mixture of a major compound and impurities is to be analyzed, it is necessary to handle each impurity separately. In some cases one of the impurities may be analyzed directly. However a particular impurity frequently absorbs at the same frequency as the other impurities thus correction factors must be added or subtracted to account for this before an analysis of the other impurities can be made. In general, the analysis is finally made from either, the absorption curves at certain prescribed frequencies, a working curve which is often a plot of transmission vs. concentration or from a Beer's Law graph. It seems the working curve method is the best for most analysis since it is usually sufficiently accurate and has the added advantage of being a time saver.

The petroleum industry seems to have monopolized the pioneer work in infrared analysis. However, such concerns as the soap industry, paint manufacturers and plastic producers are making some use of infrared. A study of the long chain fatty acids used in the soap industry would be fascinating. The oils used in

paints would present very interesting compounds for analysis. There should be no end in the application of infrared to the plastic industry or in any industry producing synthetic resinous material.

Infrared as a pure research tool has been utilized in the fascinating field of astronomy. Spectroscopists have, for years, been carrying out research in this field in order to determine the composition of the atmospheres of our neighbor planets and the more distant stars. For the most part this research has been confined to the visible and ultraviolet regions since most elements and compounds emit or absorb in this region. Recently a number of articles have been written concerning the application of infrared. An article in the Kansas City Star some weeks ago stated that astronomers of McDonald Observatory were carrying out research in order to determine the component parts of the atmosphere of Mars. They were particularly interested in finding the presence of water vapor in sufficient concentration to support life. This research was possible because of the great amount of work that has been done on our own atmosphere, in which carbon dioxide, methane, oxides of nitrogen, carbon monoxide and water vapor were found. No positive results were obtained at the observatory, possibly due to adverse atmospheric conditions. However, Dr. G. P. Kuiper of the same observatory has recently found traces of carbon dioxide. This may mean that Mars has become a dead planet. Research has also been carried out on the atmosphere of Jupiter and evidences of methane and ammonia were

discovered. Thus infrared may also become a tool in helping to unravel some of the mysteries of our universe.

Certainly infrared as an analytical tool has endless possibilities. Only a few have been cited in this chapter. The field is limited, however, to analysis in the realm of organic chemistry. This, on the other hand, is not too great a limitation because of the vast number of organic compounds whose absorption characteristics have not been investigated.

CONCLUSION

An attempt has been made in a small measure to give a rather sketchy history of spectroscopy, a brief discussion of infrared theory, some experimental techniques and procedures, methods of calibration including a discussion of the Perkin-Elmer infrared spectrometer, infrared as used in analysis and a few possible research problems that seemed interesting to the author.

The main purpose of the paper was to calibrate the Perkin-Elmer spectrometer. After careful adjustment of the working parts several absorption curves were run. These curves agreed favorably with the accepted curves for water vapor and ammonia. This indicated that the adjustment was sufficiently accurate. The calibration curves obtained by plotting known frequency against drum setting for a given spectral line were linear except toward the short wave lengths. This agreed favorably with the calibration curve furnished by the Perkin-Elmer Corporation. As far as calibration was concerned the research was a success.

There were several things gained from this research which probably should be observed in the future. First, the investigator should try to avoid radical temperature changes. These temperature changes affect dispersion as well as the behavior or the detector and recorder. Second, no matter how tedious the job, an absorption curve should be run completely through in one continuous sitting. The author found that two parts of a curve run at different times fail to fit together. Third, if at all possible an automatic recorder should be used. This is a great time saver and eliminates the necessity of continually adjusting the galvanometer for drift. It would obviously be more compact and far more economical.

ACKNOWLEDGMENT

The research for this paper would have been impossible without the generous assistance of Dr. Stuart E. Whitcomb, Major Instructor. Therefore the author wishes to thank him for his untiring efforts. The author also wishes to thank Dr. A. B. Cardwell, Head of the Department of Physics for his many helpful suggestions. Professor E. V. Floyd did much in the design and construction of some of the apparatus. To him goes my heartfelt thanks. Also, Dr. Robert McFarland contributed many useful suggestions, and to him goes the author's thanks. The author also wishes to thank all others who contributed suggestions. It is certain that without these many helping hands this research would have been exceedingly difficult.

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